9#-Lanostane-Type Triterpene Lactones from the Stem Bark of Abies veitchii

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9β-LANOSTANE-TYPE TRITERPENE LACTONES FROM THE STEM BARK OF *ABIES VEITCHII*

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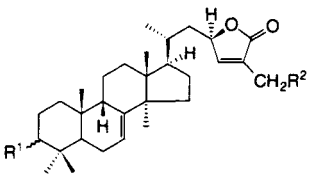
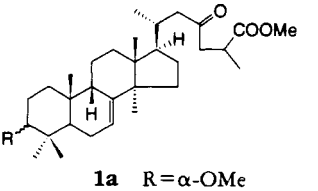
ABSTRACT.—Two new tetracyclic triterpene lactones were isolated, together with two known compounds, 3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide [**2**] and 3β-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide [**3**], from the stem bark of *Abies veitchii*. The structures of the new compounds were established as 3α-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide [**6**] and 3α-methoxylanosta-7,9(11),24-trien-26,23*R*-olide [**7**], respectively, on the basis of chemical and spectral evidence.

Abies veitchii Lindl. (Pinaceae) (Japanese name: Shirabiso) is a tall evergreen tree growing deep in the mountains from central to northern Japan (1). Our previous studies on the chemical constituents of *Abies* species have revealed a tetracyclic triterpene lactone, abieslactone [**1**] (3α-methoxy-9β-lanosta-7,24-dien-26,23*R*-olide) (2,3), from the bark and leaves of *Abies mariesii* Mast., *Abies amabilis* (Dougl.) Forbes, and *Abies procera* Rehd., a mixture of five *n*-alkyl ferulates bearing alkyl moieties from C-22 to C-26, a mixture of campesterol and β-sitosterol, 3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide [**2**] (4), 3β-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide [**3**], and 27-hydroxy-3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide [**4**] (5) from the bark of *Abies firma* Sieb. et Zucc., and abieslactone [**1**] and veitchiolide [**5**] [7β-hydroxy-3α-methoxylanosta-9(11),24-dien-26,23*R*-olide] from the bark of *A. veitchii* (6). The fact that the bark of *A. firma* contained substantial **2** and lacked abieslactone [**1**], which is the most abundant triterpenoid in the bark of both *A. mariesii* and *A. veitchii*, drew our chemotaxonomic interest in this species. During the course of our work, five groups of investigators have reported the isolation and the structure elucidation of several highly oxygenated lanostanes, 9β-lanostanes, cycloartanes, and some of their analogues from the bark and needles of *Abies alba* Mill. (7,8), the bark of *A. grandis* (9), the seeds of both *A. mariesii* and *A. firma* (10,11), and the bark and needles of *Abies sibilica* (12,13).

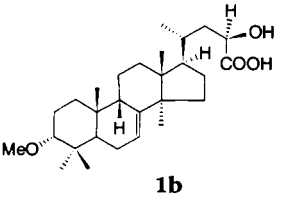
Recently, we reported that methyl esters **1a** and **2a** of two γ-keto acids and a trisnor-α-hydroxy acid **1b**, derived from compounds **1** or **2** (2), strongly inhibited both (a) incorporation of ^{32}P into phospholipids of HeLa cells cultured in the medium containing 12-*O*-tetradecanoylphorbol-13-acetate (TPA) and inorganic ^{32}P and (b) the promoting action of TPA on skin tumor formation in mice initiated with 7,12-dimethyl-



1 R^1=α-OMe, R^2=H
2 R^1=>O, R^2=H
3 R^1=β-OH, R^2=H
4 R^1=>O, R^2=OH
6 R^1=α-OH, R^2=H
6-acetate R^1=α-OAc, R^2=H



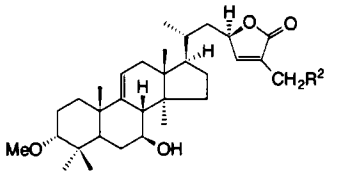
1a R=α-OMe
2a R=>O,



1b

benz[*a*]anthracene (14), although compounds **1** and **2** themselves showed no remarkable activity in the same in vitro assay.

In the search for stronger and more effective antitumor-promoting agents from plant sources, we re-examined the neutral Et_2O extract of the stem bark of *A. veitchii* and isolated two unknown triterpenoid lactones **6** and **7**, together with two known triterpene constituents **2** and **3**. This paper deals with the structure elucidation of compounds **6** and **7**.



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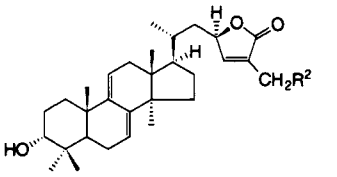

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RESULTS AND DISCUSSION

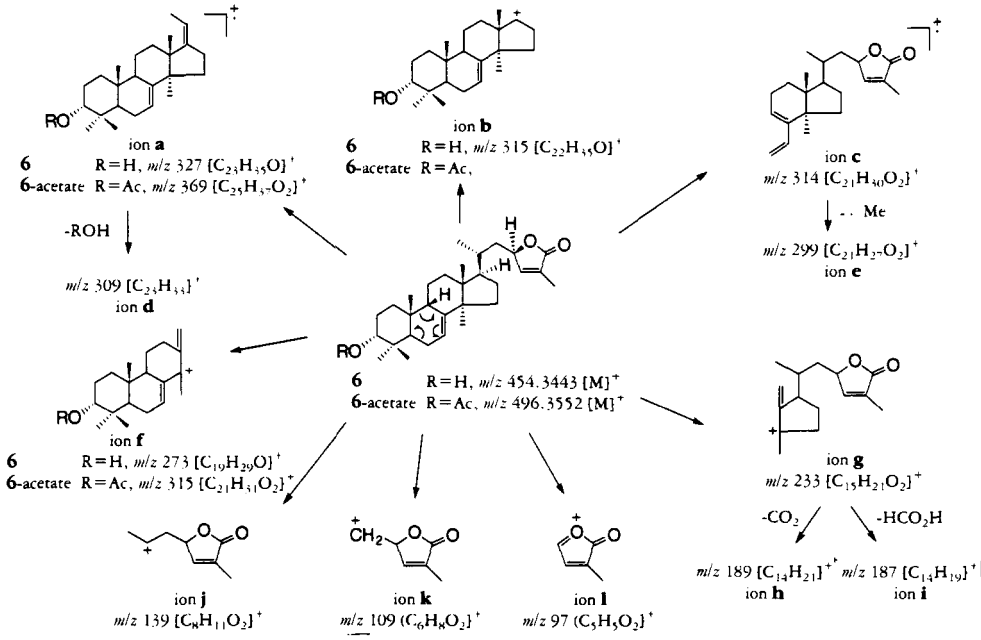
The known triterpenoids were identified by direct comparison with samples of 3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide [**2**] and 3β-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide [**3**], respectively, isolated from the bark of *A. firma* (4,5).

Compound **6**, one of two unknown compounds, gave the molecular formula $C_{30}H_{46}O_3$ ($[M]^+$ at *m/z* 454.3443) and showed positive color on the Liebermann-Burchard test. Its ir, ^{1}H-nmr (Table 1), and ^{13}C-nmr spectra (Table 2) exhibited the presence of five tertiary methyl groups, a secondary methyl group, a secondary carbinolic methine group [δ 3.43 (1H, narrow diffused t, W/2 = 6.8 Hz) and 76.32 (H-C(-OH)-)], a trisubstituted olefin bond [δ 5.55 (1H, H-7), 121.64 (=C*H*-) and 148.60 (=C<)], along with signals due to the presence of a 4-substituted 2-methyl-2-butenolide ring (closely similar to that in both compounds **2** and **3**) at δ 1.91 (3H, t, Me-27), 4.98 (1H, ddd, H-23), 7.00 (1H, H-24), 129.46 (=C<) and 149.72 (=CH-). In the DEPT and eims, compound **6** showed the same carbon composition and fragment ion peaks (Scheme 1) closely similar to those of compound **3** (5). However, ^{1}H-nmr chemical shift values for H-3, Me-19, Me-28, and Me-29 in compound **6** showed significant discrepancies of $\Delta\delta + 0.17$, $+0.08$, $+0.12$, and -0.09 ppm, respectively, in comparison with those of compound **3**, although all the other ^{1}H signals in both compounds agreed within ± 0.01 ppm. Furthermore, ^{13}C-nmr signals of C-1, C-2, C-3, C-4, C-5, C-19, C-28, and C-29 around the A ring in compound **6** showed chemical shift values considerably different from those of compound **3**, whereas all the other signals of both compounds were in good agreement. Acetylation of compound **6** yielded **6**-acetate. In the ^{1}H-nmr spectrum, compounds **6** and **6**-acetate exhibited signals attributable to 3-equatorial methine protons geminal to the hydroxyl group and acetoxy group as narrow diffused triplets (W/2 = 6.8 Hz) at δ 3.43 and 4.65, respectively, while compound **3** showed the corresponding 3-axial methine proton signal as a double doublet (J = 10.2 and 5.5 Hz) at δ 3.20 (5). All these data supported the theory that compound **6** must be the 3α isomer of **3**. The 23*R* configuration of the lactone side chain in compound **6** was estimated from cd measurements in which it gave a negative Cotton effect curve similar to those of compounds **2** and **3** (4,5). Definite proof for this assumption was obtained by the following experiment. Chromium trioxide oxidation of **6** in pyridine afforded the keto-lactone identical in all respects with compound **2**. Accord-

TABLE 1. ^{1}H-nmr Chemical Shifts of Compounds **2**, **3**, **5**, **6**, **6**-acetate, and **7** in $CDCl_3$.

Proton	Compound					
	2	**3**	**5**[a]	**6**	**6**-acetate	**7**
Me-18	0.81	0.93	0.69	0.943	0.95	0.59
Me-19	1.00	0.93	1.08	1.01	1.02	1.00
Me-21	1.01 (d, 6.5)	1.00 (d, 6.5)	1.03 (d, 6.5)	1.00 (d, 6.5)	1.00 (d, 6.5)	1.02 (d, 6.5)
Me-27	1.92 (t, 1.7)	1.91 (t, 1.7)	1.92 (t, 1.7)	1.92 (t, 1.7)	1.91 (t, 1.7)	1.92 (t, 1.7)
Me-28	1.10	0.87	0.94	0.99	0.88	0.948
Me-29	1.09	1.02	0.89	0.925	0.98	0.934
Me-30	1.03	1.02	0.83	1.03	1.02	0.87
H-2α,β	2.49 (dd, 8.5, 6.5)	—	—	—	—	—
H-3	—	3.20 (dd, 10.0, 5.5)	2.84 (t, 2.4)	3.43 (dif. t, W/2 6.8)	4.65 (dif. t, W/2 6.8)	2.84 (dif. t, W/2 6.8)
H-7	5.64 (dt, 6.5, 3.0)	5.56 (dt, 6.5, 3.0)	3.71 (td, 11.5, 5.3)	5.55 (dt, 6.5, 3.0)	5.55 (dt, 6.5, 3.0)	5.31 (br. d, 6.1)
H-11	—	—	5.31 (br. d, 6.3)	—	—	5.44 (t, 4.5)
H-23	4.98 (ddd, 9.4, 4.1, 1.7)	4.97 (ddd, 9.4, 4.1, 1.7)	4.99 (ddd, 9.4, 4.1, 1.7)	4.98 (ddd, 9.4, 4.1, 1.7)	4.97 (ddd, 9.4, 4.1, 1.7)	4.98 (ddd, 9.5, 4.1, 1.7)
H-24	7.01 (quint, 1.7)	6.99 (quint, 1.7)	7.00 (quint, 1.7)	7.00 (quint, 1.7)	7.00 (quint, 1.7)	7.01 (quint, 1.7)
3α-OMe	—	—	3.31	—	—	3.29
3α-OAc	—	—	—	—	2.05	—

[a]Data for this compound are taken from Tanaka and Matsunaga (6).



SCHEME 1. Mass spectral fragmentation of compounds **6** and **6**-acetate.

ingly, the structure of compound **6** was proved to be 3α-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide.

Compound **7**, the second new compound, gave the molecular formula $C_{31}H_{46}O_3$ ($[M]^+$ at *m/z* 466.3451) and also was positive in the Liebermann-Burchard test. Its uv and ir spectra showed the presence of an α,β-unsaturated γ-lactone ring [λ max 219 nm; ν max 1758 (shoulder) and 1740 cm^{-1}] and a heteroannular diene chromophore (λ max 236, 243.5 and 251.5 nm; ν max 1658, 897 and 815 cm^{-1}) in the molecule. In the ^1H- and ^{13}C-nmr spectra, it exhibited signals due to five quaternary methyl groups, a secondary methyl group, a vinylic methyl group deshielded with the lactone carbonyl, a secondary methoxy group attached to the C-3α position [δ 2.84 (1H, narrow diffused t, H-C(-OMe)-), 3.29 (3H, s, OMe) and 56.87 (C-3)], a $-H_2C-HC=\overset{|}{C}-\overset{|}{C}=CH-CH_2-$ moiety [δ 5.31 (1H, H-7), 5.44 (1H, H-11), 115.27 and 120.49 (each =CH-), and 142.28 and 146.23 (each =C<)], a trisubstituted olefin bond [δ 7.01 (1H, H-24), 129.40 (=C<), and 149.78 (=CH-)] lying between the lactone carbonyl [δ 174.42 (C-26)] and the methine proton attached to the etheral oxygen in the γ-lactone ring [δ 4.98 (1H, H-23)] similar to those of the 4-substituted 2-methyl-2-butenolide ring in compound **6**. Detailed analysis of 2D COSY and eims for compound **7** furnished appropriate skeletal information. In the 2D long range ^1H-^{13}C nmr spectrum, compound **7** showed cross correlation for signals of Me-18 (with C-12, C-13, C-14, and C-17), Me-19 (with C-1, C-5, C-9, and C-10), Me-21 (with C-17, C-20, and C-22), Me-27 (with C-24, C-25, and C-26), Me-28 (with C-3, C-4, C-5, and C-29), Me-29 (with C-3, C-4, C-5, and C-28) and Me-30 (with C-8, C-13, C-14, and C-15), as well as H-7 (with C-6 and C-8) and H-11 (with C-9 and C-12). The eims of compound **7** exhibited characteristic fragment ion peaks considered to arise from the cleavage of the lanosta-7,9(11)-diene skeleton at *m/z* 391 [M − Me − MeOH − CO]$^+$, 339 [ion **m**], 337 [ion **n**], 327 [ion **o**], 325 [ion **p**], 295 [ion **q**], 285 [ion **r**], and 253 [ion **s**], together with peaks due to cleavage of the side chain moiety containing a 2-methyl-2-butenolide ring

TABLE 2. ^{13}C-nmr Chemical Shifts of Compounds **2**, **3**, **5**, **6**, **6**-acetate, and **7** in $CDCl_3$ (TMS = 0).[a]

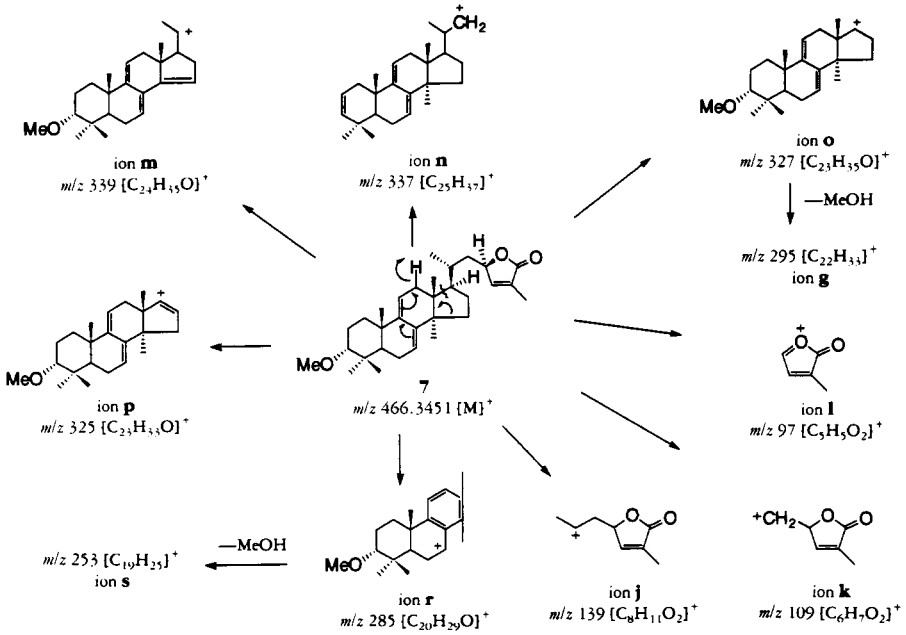
Carbon	Compound					
	2	**3**	**5**[b]	**6**	**6**-acetate	**7**
C-1	34.20	35.52	31.00	29.82	30.54	30.06
C-2	34.28	27.94	20.43	25.72	23.23	20.35
C-3	218.92	79.33	85.51	76.32	78.45	85.67
C-4	47.01	38.83	37.97	37.40	36.50	37.78
C-5	52.35	48.62	42.55	43.53	43.33	43.72
C-6	23.01	23.07	31.30	23.11	23.05	22.99
C-7	121.64	121.70	72.31	121.64	121.51	120.49
C-8	148.48	148.59	50.39	148.60	148.53	142.28
C-9	45.67	48.33	146.43	48.53	48.42	146.23
C-10	35.80	35.90	39.10	35.69	35.58	37.26
C-11	20.88	22.93	116.56	22.89	22.85	115.27
C-12	34.39	35.26	36.83	35.35	35.27	37.65
C-13	44.15	43.74	45.24	43.73	43.72	43.95
C-14	51.93	52.76	46.62	52.88	52.86	50.47
C-15	33.01	33.32	36.61	33.28	33.24	31.44
C-16	28.21	28.55	28.58	28.58	28.57	27.88
C-17	53.47	53.96	50.55	53.98	53.98	51.39
C-18	22.51	23.66	14.36	23.77	23.78	15.73
C-19	23.12	24.49	21.89	24.37	24.31	22.71
C-20	33.49	33.47	33.33	33.47	33.47	33.55
C-21	18.13	18.41	18.41	18.39	18.41	18.44
C-22	40.46	40.46	40.73	40.46	40.41	40.60
C-23	78.96	79.01	78.91	79.02	79.02	78.97
C-24	149.68	149.66	149.69	149.72	149.72	149.78
C-25	129.48	129.51	129.52	129.46	129.43	129.40
C-26	174.44	174.43	174.39	174.44	174.42	174.44
C-27	10.65	10.65	10.65	10.63	10.63	10.63
C-28	21.30	16.36	28.22	28.66	28.26	28.27
C-29	28.00	28.89	22.73	23.41	23.05	23.15
C-30	27.41	30.45	18.27	30.72	30.80	25.71
OMe	—	—	57.01	—	—	56.87
CO_2Me	—	—	—	—	21.30	—
CO_2Me	—	—	—	—	170.67	—

[a]Assignments were made by 2D ^{1}H-^{1}H COSY, 2D ^{1}H-^{13}C COSY, and 2D long-range ^{1}H–^{13}C COSY experiments.

[b]Data for this compound are from Tanaka and Matsunaga (6).

analogous to those of compounds **2** and **3** at *m/z* 139 [ion **j**], 109 [ion **k**], and 97 [ion **l**] (Scheme 2). On the other hand, the cd curve of compound **7** gave a negative Cotton effect (see Experimental) similar to those of compounds **1–6** (1, 3–5), indicative of the same side chain containing the 23*R* configuration of the lactone ring with these compounds. All these data indicated that compound **7** must be 3α-methoxylanosta-7,9(11),24-trien-26,23*R*-olide. Conclusive evidence for this structure was obtained from the following experiment. Oxidation of abieslactone [**1**] with selenium dioxide in HOAc furnished the 7,9(11),24-trien-26,23*R*-olide, which was identical in all respects with compound **7**.

To the best of our knowledge, compounds **6** and **7** have not yet been described in the literature. Further investigation on the anti-tumor-promoting activity for **6**, **7**, and their derivatives is now in progress, and results will be reported elsewhere.



SCHEME 2. Mass spectral fragmentation of compound **7**.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points were measured on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were taken in $CHCl_3$ using a Jasco DIP-140 polarimeter. Cd measurements were run in dioxane by employing a Jasco J-500 spectropolarimeter at 25°. Uv spectra were measured in EtOH on a Hitachi 150-20 spectrophotometer, and ir spectra were recorded as KBr discs with a Jasco A-100 ir spectrophotometer. ^1H- and ^{13}C-nmr spectra were obtained in $CDCl_3$ on a Varian XL-300 instrument at 300 MHz and 74.5 MHz, respectively, using TMS as internal standard. Eims were recorded at 70 eV (probe) on a Hitachi M-60 double focusing mass spectrometer. Si gel 60 (Merck, 70–230 mesh) was used for cc. Si gel PF_{254} plates (Merck, 2 mm) were employed for preparative tlc.

ISOLATION OF COMPOUNDS.—Previously, we reported that Si gel cc of the crude crystalline solid (56.5 g) deposited from the syrupy Et_2O extract of the dried stem bark of *A. veitchii* (7.9 kg) led to the isolation of abieslactone [**1**] and veitchiolide [**2**] (4). In this stage, resinous products showing closely similar tlc spots have been obtained from the intermediate fractions (fractions 135–165) eluted with $CHCl_3$ and $CHCl_3$-EtOAc (20:1). These were combined and condensed to give an amorphous solid (4.3 g), which was subjected to rechromatography on a Si gel (360 g) column. Elution with $CHCl_3$ afforded compounds **2** (182 mg) and **3** (53 mg), in order of polarity. Successive cc furnished compounds **6** (1.3 g) and **7** (28 mg) from the fractions eluted with the mixed solvent of $CHCl_3$-EtOAc (30:1) and $CHCl_3$-EtOAc (20:1), respectively.

COMPOUND **2**.—Prisms, mp 245.5–248° (EtOAc), $[\alpha]^{23}D$ +27.5° (c = 0.55, $CHCl_3$); R_f 0.56 [0.25 mm thick, solvent C_6H_6-$CHCl_3$-EtOAc (1:1:1)]; hrms $[M]^+$ 452.3288 ($C_{30}H_{44}O_3$ requires 452.3290); ir ν max cm^{-1} 3070, 3022, 2930, 2852, 1740 (α,β-unsaturated γ-lactone), 1698 (6-membered ring C=O), 1648 (C=C), 1460, 1410 (CH_2CO), 1378, 1360, 1197, 1095, 1040, 933, 878, 818 (-HC=C<); ^1H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (rel. int.) $[M]^+$ 452 (46), $[M-Me]^+$ 437 (100), $[M-Me-H_2O]^+$ 419 (13), 315 (11), 314 (12), 313 (11), 299 (20), 271 (18), 243 (20), 139 (9), 97 (37). It was identified by direct comparison (mmp, co-tlc, ir, ^1H-nmr ^{13}C nmr, and eims) with an authentic sample of 3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide isolated previously from the stem bark of *A. firma*.

COMPOUND **3**.—Needles, mp 239–241° (MeOH), $[\alpha]^{23}D$ −58.9° (c = 0.32, $CHCl_3$); R_f = 0.42 [0.25 mm thick, solvent C_6H_6-$CHCl_3$-EtOAc (1:1:1)]; hrms *m/z* $[M]^+$ 454.3449 ($C_{30}H_{46}O_3$ requires 454.3446); ir ν max cm^{-1} (KBr) 3560 (OH), 3065 (-HC=C<), 2948, 2870, 1760 (shoulder), and 1740

(α,β-unsaturated γ-lactone), 1658 (C=C), 1462, 1378, 1362, 1215, 1106, 1058, 1022, 980, 960, 878, 805 (-HC=C<); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (rel. int.) $[M]^+$ 454 (18), $[M-Me]^+$ 439 (35), $[M-H_2O]^+$ 436 (4), $[M-Me-H_2O]^+$ 421 (100), 315 (7), 314 (20), 299 (22), 273 (4), 245 (4), 227 (11), 139 (14), 97 (86). It was identified by direct comparison (mmp, co-tlc, ir, ^{1}H nmr, ^{13}C nmr, and eims) with an authentic sample of 3β-hydroxy-9β-lanosta-7,24-dien-26,23*R*-olide isolated also from the bark of *A. firma*.

COMPOUND **6**.—Prisms, mp 250–252° (MeOH/$CHCl_3$), $[\alpha]^{23}D$ −80.5° (*c* = 0.55, $CHCl_3$), R_f = 0.49 [0.25 mm thick, solvent C_6H_6-$CHCl_3$-EtOAc (1:1:1)]; hrms *m/z* $[M]^+$ 454.3443 ($C_{30}H_{46}O_3$ requires 454.3446); ir ν max cm^{-1} (KBr) 3480 (OH), 3048 (-HC=C<), 2932, 2850, 1745, and 1728 (shoulder) (α,β-unsaturated γ-lactone), 1645 (C=C), 1458, 1440, 1375, 1365, 1198, 1087, 1015, 968, 925, 862, 810 (-HC=C<); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (rel. int.) $[M]^+$ 454 (20), $[M-Me]^+$ 439 (17), $[M-H_2O]^+$ 436 (5), $[M-Me-H_2O]^+$ 421 (100), [ion **a**] 327 (2), [ion **b**] 315 (11), [ion **c** 314 (32), [ion **d**] 309 (2), [ion **e**] 299 (20), [ion **f**] 273 (7), [ion **g**] 233 (11), 227 (11), [ion **h**] 189 (3), [ion **i**] 187 (32), [ion **j**] 139 (9), [ion **k**] 109 (30), [ion **l**] 97 (55); cd (dioxane) $[\theta]_{200}$ −8100°, $[\theta]_{208}$ −26000° (trough), $[\theta]_{212}$ −22200°, $[\theta]_{220}$ −11500°, $[\theta]_{230}$ −1800°, $[\theta]_{245}$ 0°, $[\theta]_{250}$ +200°.

ACETYLATION OF COMPOUND **6**.—Compound **6** (100 mg) was dissolved in an equivolume mixture of pyridine and Ac_2O (4 ml). The mixture was kept at room temperature overnight, and subsequent workup afforded **6**-acetate (101 mg): *m/z* $[M]^+$ 496.3552 ($C_{32}H_{48}O_4$ requires 496.3552), mp 204.5–208° (MeOH/$CHCl_3$); ir ν max (KBr) cm^{-1} 2965, 2948, 2830, 1740, and 1736 (shoulder) (α,β-unsaturated γ-lactone), 1722 (OAc), 1465, 1443, 1382, 1370, 1248 (OAc), 1180, 1091, 1048, 1022, 958, 938, 867, 828; ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (rel. int.) $[M]^+$ 496.3552 (14), $[M-Me]^+$ 481 (16), $[M-HOAc]^+$ 436 (11), $[M-Me-HOAc]^+$ 421 (100), [ion **a**] 369 (1), [ion **b** − HOAc and ion **f**] 315 (7), [ion **c**] 314 (16), [ion **d**] 309 (2), [ion **e**] 299 (14), [ion **g**] 233 (8), 225 (9), [ion **h**] 189 (8), [ion **i**] 187 (20), [ion **j**] 139 (3), [ion **k**] 109 (10), [ion **l**] 97 (2).

OXIDATION OF COMPOUND **6** WITH CrO_3 IN PYRIDINE.—A solution of CrO_3 (50 mg) in pyridine (3 ml) containing 1 drop of H_2O was gradually added to a solution of compound **6** (50 mg) in pyridine (5 ml) at 10°, while stirring, and the mixture was kept at 20° for 5 h. Then, 2 drops of 10% $NaHSO_3$ solution was added to destroy excess CrO_3. Removal of the pyridine in vacuo gave a residue which was dissolved in Et_2O (30 ml), washed with 5% HCl and H_2O, and dried over Na_2SO_4. Removal of solvent yielded a solid which was purified by preparative tlc [C_6H_6-$CHCl_3$-EtOAc (1:1:1)] to give the ketone, mp 245–247° (EtOAc), 46.5 mg. The ketone was identified by direct comparison (mmp, co-tlc, ir, ^{1}H nmr, ^{13}C nmr, and eims) with an authentic sample of 3-oxo-9β-lanosta-7,24-dien-26,23*R*-olide [**2**] isolated from the stem bark of both *A. firma* and *A. veitchii*.

COMPOUND **7**.—Prisms, mp 208–209.5° (MeOH/$CHCl_3$), $[\alpha]^{23}D$ +1.4° (*c* = 0.65, $CHCl_3$); hrms *m/z* $[M]^+$ 466.3451 ($C_{31}H_{46}O_3$ requires 466.3447); uv λ max (EtOH) nm 236, 243.5, 251.5 (log ε 4.26, 4.32, 4.15) (heteroannular diene); ir ν max (KBr) cm^{-1} 2935, 2870, 1758 (shoulder), 1740 (α,β-unsaturated γ-lactone), 1658 (C=C), 1445, 1420, 1377, 1360, 1205, 1100, 1063, 940, 897, 815 (-HC=C<); ^{1}H nmr see Table 1; ^{13}C nmr see Table 2; eims *m/z* (rel. int.) $[M]^+$ 466 (100), $[M-Me]^+$ 451 (8), $[M-MeOH]^+$ 434 (14), $[M-Me-CO]^+$ 423 (5), $[M-Me-MeOH]^+$ 419 (43), $[M-Me-MeOH-CO]^+$ 391 (6), 383 (4), 365 (6), 351 (3), [ion **m**] 339 (6), [ion **n**] 337 (11), [ion **o**] 327 (4), [ion **p**] 325 (5), [ion **q**] 295 (10), [ion **r**] 285 (5), [ion **s**] 253 (19), 239 (11), 227 (9), 225 (12), 213 (8), 211 (8), 201 (13), [ion **i**] 187 (12), 171 (16), [ion **j**] 139 (3), [ion **k**] 109 (8), [ion **l**] 97 (20); cd (dioxane) $[\theta]_{200}$ −6700°, $[\theta]_{208}$ −19800°, $[\theta_{212}$ −19900° (trough), $[\theta]_{230}$ −7600°, $[\theta]_{240}$ −4900°, $[\theta]_{261}$ 0°, $[\theta]_{270}$ +450°.

SYNTHESIS OF COMPOUND **7** FROM ABIESLACTONE [**1**].—A solution of freshly sublimed selenium dioxide (20 mg) in 80% HOAc (5 ml) was gradually added to a solution of abieslactone [**1**] (40 mg) in HOAc (10 ml), and the mixture was refluxed for 1 h. After cooling, the reaction mixture was diluted with H_2O (40 ml), the resulting precipitate was extracted with Et_2O (50 ml), and the Et_2O layer was neutralized and dried with Na_2SO_4. Removal of the Et_2O afforded a residue (38 mg), which was purified by preparative tlc [C_6H_6-$CHCl_3$-EtOAc (1:1:1)] to give 3α-methoxylanosta-7,9(11),24-trien-26,23*R*-olide (30.5 mg), mp 206–208.5° (MeOH/$CHCl_3$), $[\alpha]^{23}D$ +1.4° (*c* = 1.02, $CHCl_3$), *m/z* $[M]^+$ 466.3445, uv λ max (EtOH) nm 236, 243.5, 251.5 (heteroannular diene). This compound was identified by direct comparison (mmp, co-tlc, uv, ir, ^{1}H nmr, ^{13}C nmr, and eims) with compound **7**.

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